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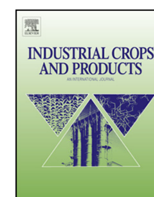

Effect of aqueous and alcoholic shear treatments on the properties of rigid plastics from wheat gluten

Thomas D. Langstraat[a,*], Koen J.A. Jansens[b,c], Jan A. Delcour[b,c], Ignaas Verpoest[d,f], Peter Van Puyvelde[e,f], Bart Goderis[a,c,f]

[a] Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium
[b] Laboratory of Food Chemistry and Biochemistry, KU Leuven, Kasteelpark Arenberg 20, 3001 Leuven, Belgium
[c] Leuven Food Science and Nutrition Research Centre (LFoRCe), KU Leuven, Kasteelpark Arenberg 20, 3001 Leuven, Belgium
[d] Department of Materials Engineering, KU Leuven, Kasteelpark Arenberg 44, 3001 Leuven, Belgium
[e] Department of Chemical Engineering, KU Leuven, Willem de Croylaan 46, 3001 Leuven, Belgium
[f] Leuven Material Research Centre (Leuven-MRC), KU Leuven, Belgium

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ABSTRACT

Two procedures conducive to blending wheat gluten with other polymers in view of enhancing the mechanical properties of rigid gluten materials, were investigated. Method 1 involved extrusion of an aqueous gluten dough at 30–110 °C. In method 2, gluten was processed in 70% ethanol at temperatures ≤130 °C in a pressurised reactor. After solvent removal, the dried powders were compression moulded into products exhibiting fewer defects than gluten moulded directly without any pre-treatment, suggesting that application of either method improved polymer flow. In temperature regimes where little or no crosslinking occurred during the shear treatments, the mechanical properties of compression moulded samples were also better than those of directly moulded gluten. Further improvements were observed when glutenin aggregates depolymerised via breaking of disulfide bonds. This occurred in method 2 at temperatures exceeding 90 °C. Materials processed via method 2 at 110 °C displayed a high level of strain hardening in compression tests, which suggests an increase in molecular entanglements.
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1. Introduction

Sustainability concerns are largely driving research efforts into alternatives to petroleum based plastics (Ramani, 2012). Some proteins are cheap, abundant resources that are interesting in this context (Cuq et al., 1998; Verbeek and van den Berg, 2010). The storage protein of wheat, wheat gluten (WG), can be processed into plastic materials with a wide array of properties (Lagrain et al., 2010). Whilst academic interest in this topic is substantial, inferior mechanical performances with respect to established synthetic plastics as well as processing related challenges have prevented protein-based materials from garnering any significant commercial success.

WG consists of a heterogeneous mix of gliadin and glutenin proteins, which are distinguished by their relative solubility in aqueous alcohols. Gliadins are extractable in aqueous ethanol. They are single chain peptides with molecular weight (MW) of 30 k–60 k. Glutenins are unextractable in aqueous ethanol. They are large polymeric protein aggregates that consist of single chain glutenin subunits (GS) covalently linked by interchain disulfide (SS) bonds (Delcour et al., 2012). Heat treatment of WG induces protein crosslinking which can involve direct oxidation of free thiol (SH) groups (present in glutenin) to form additional SS bridges, but proceeds chiefly via an interchange mechanism in which intramolecular SS bonds are broken and reformed as network forming intermolecular SS bonds (Schofield et al., 1983). Gliadins, which contain no free SH groups, are incorporated into the network via the latter mechanism (Lagrain et al., 2008). During heat treatments of WG involving mechanical mixing, shear mediated scission of SS bonds can yield reactive thiyl radicals (Auvergne et al., 2008; Morel et al., 2002). Whilst the aggregated structure and high MW likely make a significant contribution to the promising properties of WG

Abbreviations: DTT, dithiothreitol; GS, glutenin subunits; HPLC, high-performance liquid chromatography; MW, molecular weight; PTFE, polytetrafluoroethylene; SDS, sodium dodecyl sulfate; SDSEP, extractable protein with SDS containing medium; SE-HPLC, size-exclusion high-performance liquid chromatography; SH, sulfhydryl; SS, disulfide; WAXS, wide-angle x-ray scattering; WG, wheat gluten.

* Corresponding author.
E-mail address: thomas.langstraat@chem.kuleuven.be (T.D. Langstraat).

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based materials, they also lead to a very high melt viscosity, which limits the processability of the proteins in the dry state.

At room temperature WG proteins are glassy. They convert to a rubbery state at the glass transition temperature (T_g). T_g is highly sensitive to moisture content or the presence of other plasticisers (Toufeili et al., 2002). Many studies have demonstrated that, with sufficient plasticisation, typically achieved by addition of glycerol (20–40 wt%), WG can easily be processed using traditional polymer techniques such as extrusion (Chantapet et al., 2013; Ullsten et al., 2009), compression (Sun et al., 2008; Zárate-Ramírez et al., 2011) and injection moulding (Cho et al., 2011). Injection moulding a WG glycerol premix leads to thermosetting and the formation of rubbery products. This approach is unfortunately not suitable for producing rigid, glassy WG products as the viscosity of non-plasticised WG is too high. Glassy WG materials are therefore produced almost exclusively by high temperature compression moulding of WG powders (Lagrain et al., 2010). Reported mechanical properties for glassy WG are comparable to those of epoxy resins, with samples showing high stiffness (3.5 GPa) and strength (50 MPa) but only withstanding low deformation before brittle failure (Jansens et al., 2013b). Various attempts have been made to reduce the brittleness of WG based materials. These have included blending with more ductile polymers (Diao et al., 2014; Dicharry et al., 2006; John et al., 1998) and introducing structural modifiers such as crosslinkers (Woerdeman et al., 2004) or reducing agents (Jansens et al., 2014, 2013a). With correct modification gluten blends may be able to provide an alternative to toughened synthetic commodity plastics such as high-impact polystyrene (HIPS). To avoid compromising the stiffness of the end product by using plasticisers which cannot be removed, blending is usually carried out with the aid of water or organic solvents which can easily be removed after blending and prior to compression moulding. When designing a procedure for processing proteins it is important to take into consideration that they are complex macromolecules consisting of a sequence of amino acids which give the protein a native folded conformation that is mainly dictated by non-covalent hydrogen bonds, hydrophobic interactions and weak van der Waals forces, and as such is only marginally stable (Batchelor et al., 2004). A blending procedure that involves solvents, high temperature and shear forces will, thus, almost certainly have an impact on the native protein structure.

In this paper two different methods for processing WG are explored. In method 1, extrusion of WG is carried out using a low level of water to plasticise the protein. In method 2, WG is mixed in 70% ethanol, whereby a solution/suspension system is obtained (soluble gliadins and insoluble glutenins). Both routes are executed at high temperature and with mechanical mixing that would be conducive to blending proteins with polymers or additives that may have a high T_g or melting point, whilst keeping in mind that extensive protein degradation should be avoided. After exposure to the two proposed processing methods, plasticiser removal and powder milling, rigid plastic materials were compression moulded from the WG proteins. Particular focus was put on relating mechanical properties of the rigid materials to protein structural changes occurring during the aqueous and alcoholic thermal treatments.

2. Experimental section

2.1. Materials

Commercial WG with a protein content of 79% (dry basis) was obtained from Tereos Syral (Aalst, Belgium). Protein content was determined on a Dumas protein analysis system (EAS Variomax N/CN, Elt, Gouda, The Netherlands) using an adaptation of the AOAC Official Method (AOAC 1995). A conversion factor of 5.7 was used to calculate protein from nitrogen content. All chemicals, solvents and reagents were from Sigma–Aldrich (Steinheim, Germany) unless specified otherwise and were at least of analytical grade.

2.2. Extrusion

WG was mixed with deionised water at a ratio of 70:30 (w/w) in a kitchen mixer (SEB Optimo Power, SEB, Selongey, France) until homogeneous dough was obtained. The dough was fed into a DSM (DSM Xplore, Geleen, The Netherlands) Micro 15 cc Extruder (vertical, co-rotating, twin-screw extruder) equipped with a recirculation channel which facilitates control over extrusion time. Extrusion was carried out for 5 min under regular air atmosphere at a screw speed of 100 rpm (unless specified otherwise). Extrusion temperature was varied from 30 to 110 °C. After 5 min the valve which controls whether the material recirculates or exits via the die was opened and the resulting stringy extrudates were cut into pellets and dried over 48 h in a vacuum oven at 40 °C. Samples were then ground in a laboratory mill (IKA, Staufen, Germany) and sieved through a 250 μm sieve.

2.3. Mixing in aqueous alcohol

WG (40 g) was mixed in 500 ml 70% (v/v) ethanol in water to achieve a good suspension, which was then transferred to a 1 l pressure reactor (Büchiglasuster, Uster, Switzerland). The reactor was equipped with an external heating jacket, the temperature (T_{set}) of which was controlled thermostatically. The temperature inside the reactor ($T_{internal}$) was monitored using a thermocouple. After transferal of the suspension, the reactor was hermetically sealed, mixing was commenced at 200 rpm and T_{set} was increased. Once $T_{internal}$ approached the desired mixing temperature, T_{set} was carefully adjusted to ensure that $T_{internal}$ remained constant to within +/− 2 °C of the desired mixing temperature. Mixing was then carried out for 60 min. Finally T_{set} was changed to 20 °C and after $T_{internal}$ dropped below 60 °C the suspension was removed from the reactor via a valve in the base of the vessel. Ethanol was removed by rotary evaporation and the remaining mixture freeze dried. Samples were ground in a laboratory mill (IKA, Staufen, Germany) and sieved through a 250 μm sieve. The temperatures reported in the results section refer to $T_{internal}$. At 110 °C and 130 °C the internal pressure in the reactor was around 2.5 and 4.5 bar respectively.

2.4. Protein extractability in SDS containing medium

Changes in protein size distribution and extractability in sodium dodecyl sulfate (SDS) containing medium were evaluated with size-exclusion high-performance liquid chromatography (SE-HPLC) as in Jansens et al. (2011). In each case, samples (1.0 mg protein) were extracted with sodium phosphate buffer (1.0 ml, 0.05 M, pH 6.8) containing 2.0% (w/v) SDS. Samples were extensively vortexed, shaken (60 min, 150 rpm) and centrifuged (10 min, 10,000 g). Protein extractability under reducing conditions was determined using the same procedure but now with addition of urea (2.0 M) and 1.0% (w/v) dithiothreitol (DTT) to the sodium phosphate buffer. To prevent re-oxidation, reduced samples were prepared under a nitrogen atmosphere. SE-HPLC was carried out on an LC-2010HT system (Shimadzu, Kyoto, Japan). Extracts were filtered and loaded (60 μl) on a BioSep SEC-S4000 column (300 × 7.8 mm, Phenomenex, Torrance, CA, USA) and eluted with acetonitrile/water (1:1, v/v) containing 0.05% (v/v) trifluoroacetic acid. The flow rate was 1.0 ml/min and the column temperature 30 °C. Protein elution was monitored at 214 nm. The amount of protein extractable in SDS containing medium (SDSEP) was calculated from the area under the HPLC elution curves and expressed as a percentage of the peak area of unheated WG extracted under reducing conditions. The

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